

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 293 479 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 158(3) EPC

(43) Date of publication:

19.03.2003 Bulletin 2003/12

(51) Int Cl.7: **C01G 1/00**

(21) Application number: **00977887.9**

(86) International application number:
PCT/JP00/08266

(22) Date of filing: **24.11.2000**

(87) International publication number:
WO 01/096242 (20.12.2001 Gazette 2001/51)

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**

(30) Priority: **12.06.2000 JP 2000175306**

(71) Applicant: **JAPAN SCIENCE AND TECHNOLOGY
CORPORATION**
Kawaguchi-shi, Saitama 332-0012 (JP)

(72) Inventors:

- **DOMEN, Kazunari**
Kanagawa-ken 228-0803 (JP)

• **LI, Byonjin**

Tokyo 194-0001 (JP)

• **NOMURA, Junko**

Yamato-shi Kanagawa-ken 242-0029 (JP)

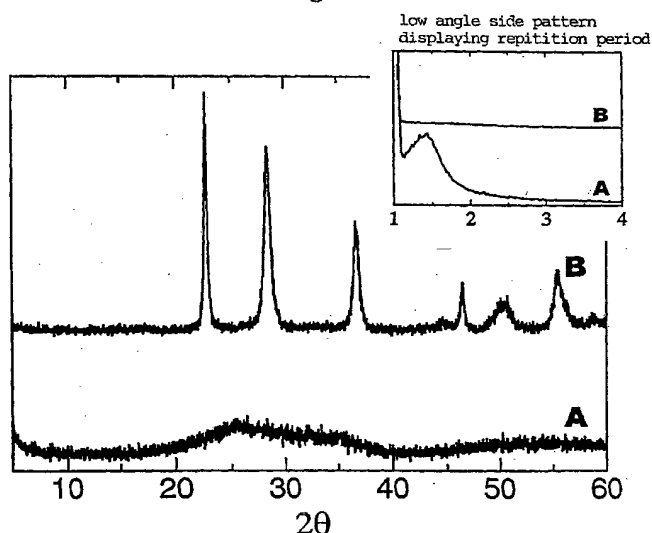
(74) Representative: **Albrecht, Thomas, Dr.**
Kraus & Weisert,
Thomas-Wimmer-Ring 15
80539 München (DE)

(54) **MESO-POROUS TRANSITION METAL OXIDE HAVING CRYSTALLIZED PORE WALL AND
METHOD FOR PREPARING THE SAME**

(57) A meso porous transition metal oxide comprising one or more transition metal oxides, wherein the metal is selected from the group consisting of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Zr, Nb, Mo, Ru, Cd, In, Sn, Sb, Hf, Ta, W and Re, and the pore wall of the meso

pore thereof has a crystalline structure; and a method for preparing the meso porous transition metal oxide, characterized as comprising a step of carrying out a secondary calcination at 600-800°C for 10 minutes to 10 hours.

Fig.2



B: Secondary calcination 650°C, 1 hour (crystallized)
A: Previous calcination(450°C), 20 hours (amorphous)

Description

FIELD OF THE INVENTION

[0001] The present invention relates to a meso-porous transition metal oxide characterizing the pore wall of meso pore have a crystalline structure, particularly, the crystalline structure is maintained over whole primary particles, further relates to the method for preparation for said meso-porous transition metal oxide. In the present invention, the term of meso pore means the fine pore whose pore size is from 2nm to 50nm especially, smaller than 15nm, further, means the fine pore (meso pore) characterizing that the nitrogen adsorption isotherm line raises rapidly at the closer region of P/P_0 0.6 and becomes flat at over than P/P_0 0.8 region.

BACK GROUND OF THE INVENTION

[0002] It is well-known that the surfactant organizes silica into a variety of meso-porous structures through the mediation of electro static force, hydrogen bond, covalent bond or van der Waals interactions. The pore wall of meso-porous structural silica prepared by using the surfactant as a matrix is amorphous. Said method to form meso-porous structures is tried to apply to non-silica oxides. Due to a sporadic success, said trial is extended to the material which applies the physical characteristics such as electron transfer or magnetic interactions.

[0003] Regarding to the oxide such as TiO_2 , ZrO_2 , Al_2O_3 , Nb_2O_5 , Ta_2O_5 , WO_3 , HfO_2 , SnO_2 or the metal oxide including mixed oxide such as $SiAlO_{3.5}$, $Si_2AlO_{5.5}$, $SiTiO_4$, $ZrTiO_4$, Al_2TiO_5 or ZrW_2O_8 , there is a paper reporting that the material which has meso porous structure having thermally stable and ordered pore of relatively large size (up to 140Å, 14nm) and which can be broadly applied is obtained [NATURE, Vol.396, 152-155 (1998); hereinafter shortened to Paper A].

[0004] In said paper, the following items are reported. Namely, the product original material is prepared by dissolving 1g of polyalkyleneoxide block copolymer [$HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2CH_2OCH_2CH_2O)_{20}H$, hereinafter shortened to $EO_{20}PO_{70}EO_{20}$; Pluronic P-123, product of BASF] is dissolved into 10g of ethanol (EtOH). To this solution 0.01mol of the respective inorganic chloride precursor is added with vigorous stirring for half hour so as to obtain sol solution, said sol solution is poured into an open Petri dish, then placing it in the atmosphere of 40°C for 1 to 7 days to make it gelation. During said gelling process, the inorganic chloride precursor (chloride of transition metal) is hydrolyzed and polymerized, and organized to metal oxide network structure. Or, material to be coated, such as substrate is dipped into said sol solution, coated film is formed on the surface of substrate and a gel product is prepared according to above mentioned reaction. In this case, it is reported that the ap-

pearance of all as made products are transparent except the appearance of product derived from WO_3 is dark blue.

[0005] Then, it is reported that the obtained gel product is heated at 400°C for 5 hours and the surfactant is removed by this calcination process, and ZrO_2 having meso structure corresponding to the matrix of $EO_{20}PO_{70}EO_{20}$ is obtained.

[0006] And the authors of said paper are guessing that the formation of said structure is formed by way of mechanism which combines the self organization of the block copolymer and the complexation of inorganic species (segment of alkylene oxide forms crown ether type complex).

[0007] Further, said paper reports that although the pore wall of meso porous silica is amorphous, above mentioned pore wall of meso structure has a structure possessing crystalline domain of nano size (up to 30Å, 3nm) in a comparatively thick amorphous wall.

[0008] Furthermore, in said paper, the sequence of atom (lattice surface) and chemical component (in which metal oxide is governable) of net work structure are considered by an X ray diffraction method (XRD) or by an energy dispersive type X ray spectroscopic method (EDX), and the ordered semi crystalline inorganic stereo network characteristic of meso structure is investigated by a conventional transmission electron microscope, and authors explain that the pore wall has a structure characterized that the nano crystalline smaller than 30Å is embedded in an amorphous matrix.

[0009] Still further, regarding to the pore, by considering the N_2 adsorption/desorption isothermal characteristic, type of pore, porosity (smaller than approximately 50%) and pore size (50-140Å) are investigated. According to the investigation by the inventors of the present invention, since the pore wall described in said paper is composed of amorphous matrix, it is obvious that said pore wall has problems that thermal or hydrothermal stability is comparatively small and physically fragile.

[0010] The inventors of the present invention thought out that the method to dissolve above mentioned problems which meso size structure composed of well known metal oxide has is to make the metal oxide composing of pore wall crystallized.

[0011] Therefore, the object of the present invention is to provide a meso porous transition metal oxide characterized that the pore wall maintains crystalline structure over whole primary particles, and is to provide a method for preparation of said meso porous transition metal oxide having said crystalline structure.

DISCLOSURE OF THE INVENTION

[0012] The first one of the present invention is the meso porous transition metal oxide characterized that the pore wall of meso pore has a crystalline structure. Desirably, the present invention is the meso porous tran-

sition metal oxide characterized that the crystalline structure is maintained over whole primary particles, more desirably is the meso porous transition metal oxide characterized that the pore wall of meso pore has the crystalline structure from which diffraction peak by electron beam diffraction is observed, further desirably is the meso porous transition metal oxide characterized that the nitrogen adsorption isotherm line raises rapidly at the closer region of P/P_0 0.6 and becomes flat at over than P/P_0 0.8 region. Still further desirably, the present invention is the meso porous transition metal oxide wherein the metal which composing of transition metal oxide is one or more than two kinds of metal elements selected from the group consisting of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Zr, Nb, Mo, Ru, Cd, In, Sn, Sb, Hf, Ta, W and Re.

[0013] The second one of the present invention is the method for preparation of meso porous transition metal oxide characterized that the pore wall of meso pore has a crystalline structure comprising, adding a transition metal salt which is a precursor of the transition metal oxide into the solution prepared by dissolving a polymer surfactant into organic solvent and dissolving, transforming said transition metal salt to a sol solution by hydrolysis and polymerization, obtaining an aimed gel state product from said sol solution and carrying out a previous calcination on said product at the temperature of $400 \pm 50^\circ\text{C}$ for 5-20 hours, then carrying out a secondary calcination at the temperature of $600-800^\circ\text{C}$ for 10 minutes to 10 hours. Desirably, the second one of the present invention is the method for preparation of meso porous transition metal oxide characterizing that the pore wall of meso pore has a crystalline structure, wherein the transition metal salt which is a precursor of the transition metal oxide is selected from a chloride, a nitrate of at least one metal element selected from the group consisting of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Zr, Nb, Mo, Ru, Cd, In, Sn, Sb, Hf, Ta, W and Re or a voluntary mixture of them.

BRIEF ILLUSTRATION OF THE DRAWINGS

[0014]

Fig.1 is the graph showing the relationship between the calcination temperature (removal of surfactant) of the gel product of Example 1, weight reduction (TGA:%) and exothermic (DTA).

Fig.2 is the graph showing the X-ray diffraction pattern of the meso porous transition metal oxide of Example 1.

Fig.3 is the graph showing N_2 adsorption isotherm line of product (A) obtained by the previous calcination process (400°C , for 20 hours) and product (B) obtained after the secondary calcination process (650°C , for 1 hours).

Fig.4 is the graph showing the distribution of fine pores of product (A) obtained by the previous calci-

nation and product (B) obtained after the secondary calcination of Example 1.

Fig.5 is the electron beam diffraction pattern (picture) of whole primary particles after the secondary calcination of Example 1.

Fig.6 is the transmission electron microscope (TEM) image (picture) of the product after the secondary calcination of Example 1.

Fig.7 is the graph showing the X-ray diffraction pattern of meso porous transition metal oxide showing the crystalline structure of ZnNb_2O_6 of Example 2. Fig.8 is the graph showing N_2 adsorption isotherm line of transition metal oxide of after the previous calcination and after the secondary calcination of Example 2.

Fig.9 is the graph showing the X-ray diffraction pattern of meso porous transition metal oxide showing the crystalline structure of $\text{Zr}_6\text{Nb}_2\text{O}_{17}$ of Example 3. Fig.10 is the graph showing N_2 adsorption isotherm line of transition metal oxide of after the previous calcination and after the secondary calcination of Example 3.

[0015] The present invention will be illustrated more in detail according to the following description.

A. As a surfactant which is used for the formation of nano size fine pores of the present invention, the surfactant which is used in above mentioned paper can be used. That is, polyalkylene oxide block copolymer composed of oligomer (containing polymer) of ethylene glycol, oligomer (containing polymer) of polypropylene glycol and the compound prepared by etherification of an end group of said block copolymer using alcohol or phenol can be mentioned. These compounds are the desirable surfactant, because the toxicity of these compounds is very low. Further, besides these compounds, the compound which is used as the conventional template compound to form nano size pores can be used.

The mole ratio of above mentioned surfactant to the metal salt forming above mentioned metal oxide is approximately from 40 to 60, and this ratio is not essentially different from that of the case disclosed in afore mentioned public known paper.

The total volume of fine pores of metal oxide which can be obtained depends on the content and the size of nonionic surfactant contained in the starting solvent. Still more, the channel structure of meso pore size or the size depend on the molecule weight or size of above mentioned surfactant or non-aqueous solvent. Therefore, the amount and the size of the organic molecule to be used in the solvent are selected so that the desired meso pore-total volume and meso pore channel size can be obtained. As the water insoluble compound, besides alcohols such as ethanol, oxygen containing

organic solvent such as ether or acetone, further, pyridine or aniline can be used.

B. As the transition metal salt, which is a precursor forming above mentioned transition metal oxide, the compound selected from the group consisting by chloride or nitride of above mentioned metal and voluntarily mixture of them can be used. Especially, the chloride is used as the desirable material.

[0016] Said transition metal oxide precursor is hydrolyzed and polymerized and transformed to the metal oxide network structure. The pre organization of meso structural fine pore systematized under the interaction with above mentioned surfactant is formed (fine pores are formed according to the removal of the surfactant by calcination).

[0017] As the transition metal, at least one element selected from the group consisting of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Zr, Nb, Mo, Ru, Cd, In, Sn, Sb, Hf, Ta, W and Re can be used.

EXAMPLE

Example 1

Preparation of meso porous metal oxide

[0018] 1g of nonionic surfactant (Pluronic L-121, L-101, L-61, L-64, L-31, P-123, P103, P-85, F-108, F-88 or F-68) and totally 0.005 to 0.015 mol of chloride of tantalum and niobium are added to 10g of normal alcohol (methanol, ethanol, propanol, butanol or hexanol) with vigorous stirring at the room temperature for 30 minutes and obtain sol solution. Said sol solution is stood at 40°C for 1 to 24 days and the transparent specimen (gel) generates.

[0019] The generated transparent specimen is calcined (previous calcination) at the temperature of 400°C under the constant flow of the air for 5-20 hours. Then the calcination temperature is elevated to 650°C and the calcination is continued another 1 hour (secondary calcination) and the aimed product is obtained.

[0020] In the calcination process of above mentioned transparent specimen, the relationship between weight reduction (TGA:%), exothermic (DTA) and the calcination temperature (°C) is shown in Fig.1. The exothermic peak at 300°C is the peak of calcination of surfactant. And, the small peak at 680°C is the peak of crystallization of pore wall, that is, the peak means the crystallization exothermic peak.

[0021] Fig.2 indicates the X-ray diffraction pattern of the meso porous transition metal oxide showing that the pore wall of obtained meso pore has crystalline structure.

[0022] In Fig.2, A is the X-ray diffraction pattern of product after the previous calcination (400°C, 20 hours amorphous). Any diffraction peak is not observed, and indicates that the pore wall is amorphous state. While,

B is the X-ray diffraction pattern of product after the secondary calcination (650°C, 1 hour, crystallized). The small graph in the upper part is the low-angle side pattern displaying repetition period.

[0023] In Fig.3, N₂ adsorption isotherm lines of product after the previous calcination (A) and after the secondary calcination (B) are shown. When N₂ adsorption isotherm line A is compared with N₂ adsorption isotherm line B, from the adsorption characteristic of the product after second calcination, it is obviously understood that the radius of fine pore is large, and from the rising characteristic, it is understood that the product has uniform fine pores.

[0024] Fig.4, is the distribution of fine pores of product after the previous calcination (A) and after the secondary calcination (B) displayed by fine pore size, and is corresponding to the characteristic of Fig.3.

[0025] Fig.5 shows the whole electron beam diffraction pattern of product (primary particles) after the secondary calcination (B), and it is obviously understood that the whole is crystalline structure.

[0026] Fig.6 is a transmission electron microscope (TEM) picture of 800,000 magnifications, and the diffraction pattern of long period can be observed. And from this TEM picture it is also obviously understood that the whole pore wall is crystalline structure.

[0027] The specimens of the product are respectively exposed in the following conditions, namely, 600°C for 20 hours, hydrothermal atmosphere of 200°C for one day and 500kg/cm² for 10-20 hours. Then thermal stability, hydrothermal stability and pressure stability are measured by checking whether the original fine pore structure and pore wall characteristic are maintained as is or not. And the results show that the fine pores structure and pore wall characteristic are maintained stable.

Example 2

Preparation of meso porous metal oxide

[0028] 1g of EO₂₀PO₇₀EO₂₀ (Pluronic P-123), further totally 0.005 to 0.015 mol of chloride of zinc and niobium are added to 10g of normal alcohol (ethanol, or butanol) with vigorous stirring at the room temperature for 30 minutes and obtain sol solution. Said sol solution is stood at 40°C for 1 to 30 days and the transparent specimen (gel) generates. The generated transparent specimen is calcined (previous calcination) at the temperature of 400°C under the constant flow of the air for 5-20 hours. Then the calcination temperature is elevated to 600°C and the calcination is continued another 10 minutes to 1 hour (secondary calcination) and the aimed product is obtained.

[0029] In Fig.7, X-ray diffraction pattern of obtained meso porous transition metal oxide having the crystalline structure of ZnNb₂O₆ is shown, and in Fig.8, N₂ adsorption isotherm lines of transition metal oxide of after the previous calcination and after the secondary calci-

nation are shown.

Example 3

Preparation of meso porous metal oxide

[0030] 1g of $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (Pluronic P-123), further totally 0.005 to 0.015 mol of chloride of zirconium and niobium are added to 10g of ethanol with vigorous stirring at the room temperature for 30 minutes and obtain sol solution. Said sol solution is stood at 40°C for 1 to 30 days and the transparent specimen (gel) generates.

[0031] The generated transparent specimen is calcined (previous calcination) at the temperature of 400°C under the constant flow of the air for 5-20 hours. Then the calcination temperature is elevated to 750°C and the calcination is continued another 30 minutes to 1 hour (secondary calcination) and the aimed product is obtained.

[0032] In Fig.9, X-ray diffraction pattern of meso porous transition metal oxide having the crystalline structure of obtained $\text{Zr}_6\text{Nb}_2\text{O}_{17}$ is shown, and in Fig.10, N_2 adsorption isotherm lines of transition metal oxide of after the previous calcination and after the secondary calcination are shown.

[0033] As mentioned above, tantalum and niobium mixed oxide, ZrNb_2O_6 and $\text{Zr}_6\text{Nb}_2\text{O}_{17}$ are illustrated. And it is natural that above mentioned method can be applied to the preparation of meso porous transition metal oxide characterizing that the pore wall of meso pore has a crystalline structure which is composed of single transition metal oxide consisting of above mentioned complex oxide and single or complex oxide of transition metal excepting mentioned above.

POSSIBILITY FOR THE INDUSTRIAL USE

[0034] As mentioned above, the present invention involves an excellent effect which makes the provision possible, namely, to provide the material composed of transition metal oxide characterizing that the pore wall of meso pore has a crystalline structure, and having meso pore of uniform size and stable structure. The characteristic of uniform and stable meso pore which said material has can be broadly used in various fields, for example, uses in chemical field such as molecular sieving, catalyst having selective function or catalyst carrier and uses in development of various functional materials which use the special characteristics realized by the structural feature of meso size.

Claims

1. A meso porous transition metal oxide characterizing that the pore wall of meso pore has a crystalline structure.

2. The meso porous transition metal oxide of claim 1, wherein crystalline structure is maintained over whole primary particles.

3. The meso porous transition metal oxide of claim 1 or claim 2, wherein the pore wall of meso pore has the crystalline structure from which diffraction peak by electron beam diffraction is observed.

4. The meso porous transition metal oxide according to any one of claims 1 to 3, wherein the nitrogen adsorption isotherm line raises rapidly at the closer region of P/P_0 0.6 and becomes flat at over than P/P_0 0.8 region.

5. The meso porous transition metal oxide according to any one of claims 1 to 4, wherein the metal which composing of transition metal oxide is one or more than two kinds of metal elements selected from the group consisting of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Zr, Nb, Mo, Ru, Cd, In, Sn, Sb, Hf, Ta, W and Re.

6. A method for preparation of the meso porous transition metal oxide characterized that the pore wall of meso pore has a crystalline structure comprising, adding a transition metal salt which is a precursor of the transition metal oxide into the solution prepared by dissolving a polymer surfactant into organic solvent and dissolving, transforming said transition metal salt to a sol solution by hydrolysis and polymerization, obtaining an aimed gel state product from said sol solution and carrying out a previous calcination on said product at the temperature of $400 \pm 50^\circ\text{C}$ for 5-20 hours, then carrying out a secondary calcination at the temperature of $600-800^\circ\text{C}$ for 10 minutes to 10 hours.

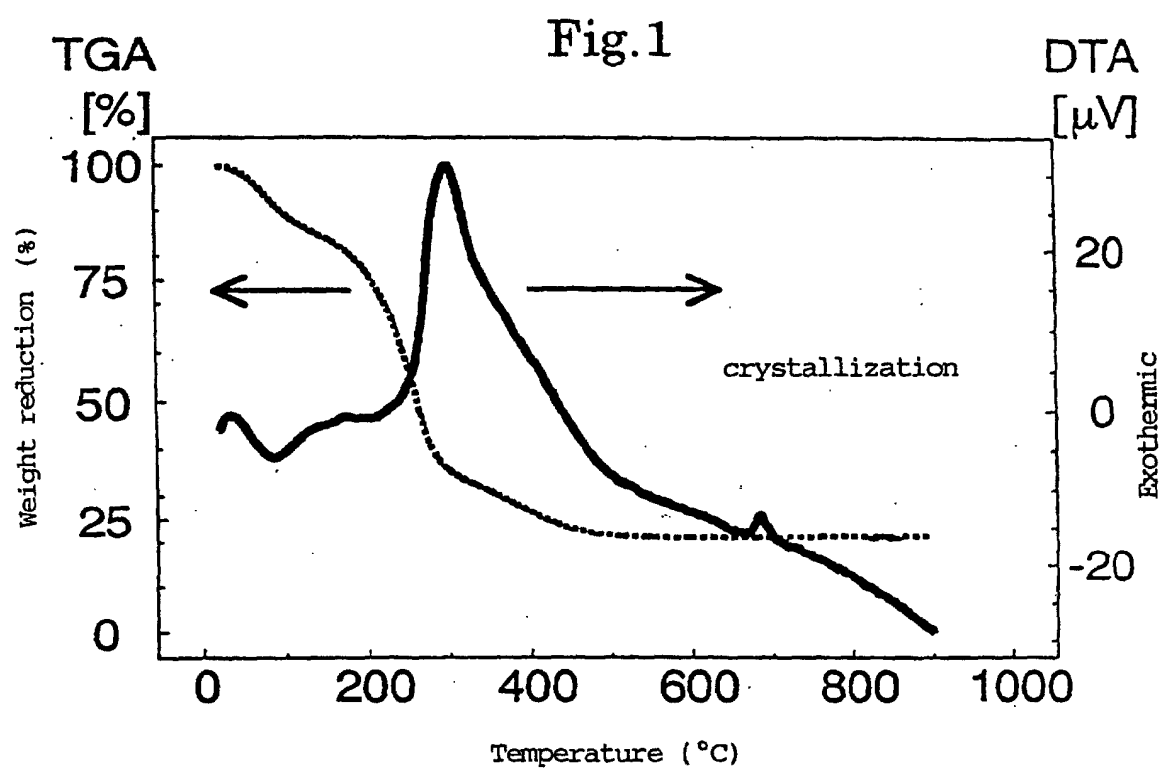
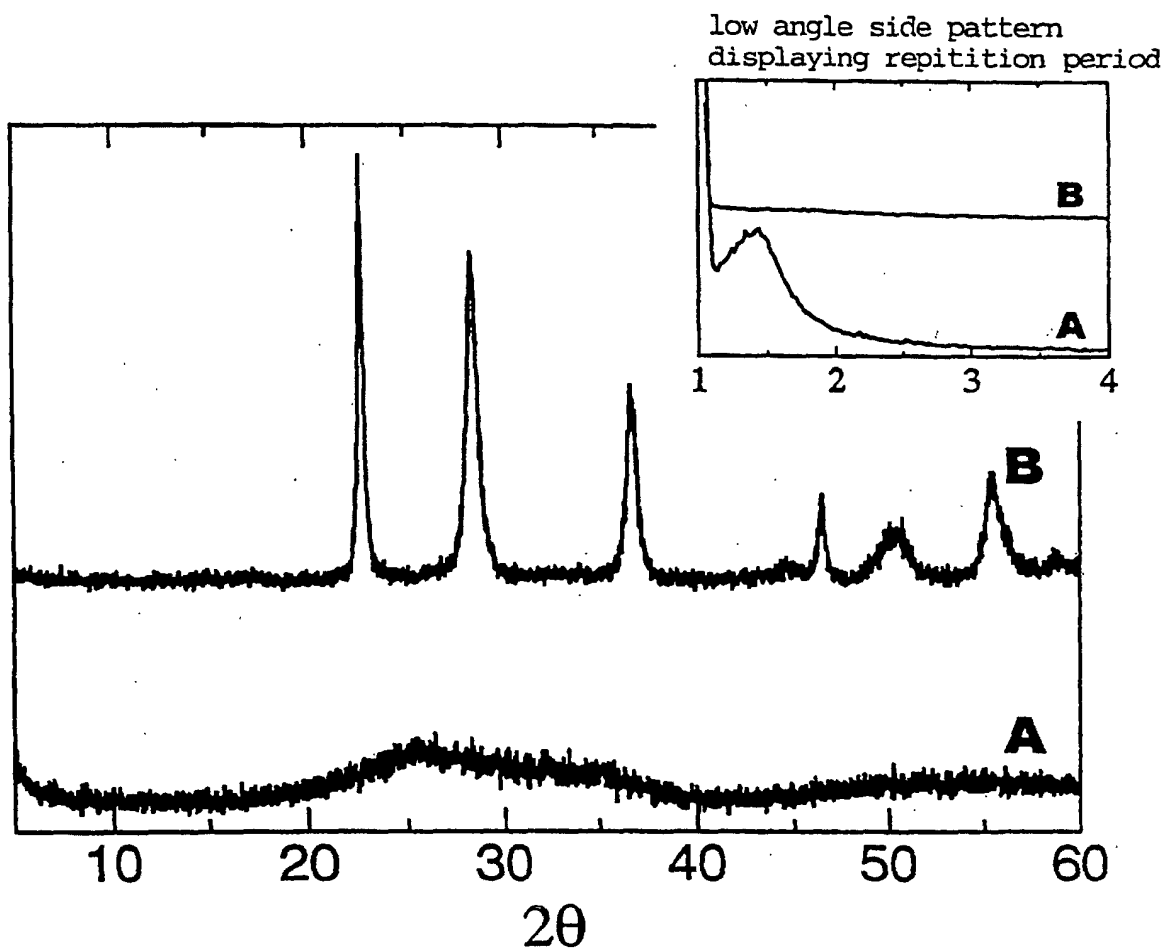


Fig.2



B: Secondary calcination 650°C, 1 hour (crystallized)

A: Previous calcination(450°C), 20 hours (amorphous)

Fig.3

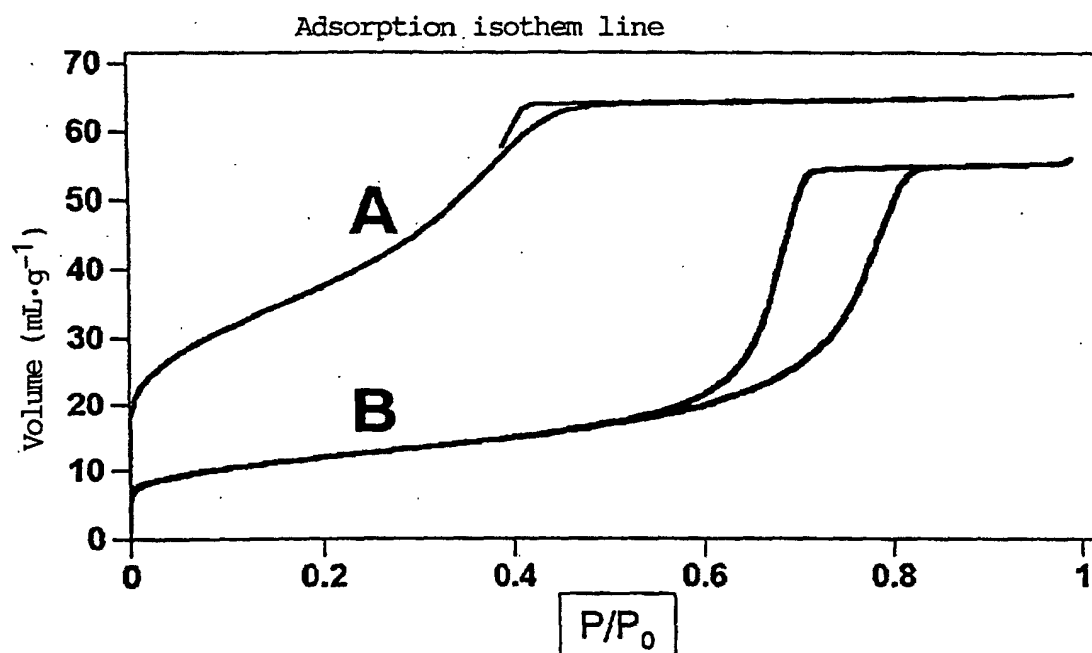


Fig.4

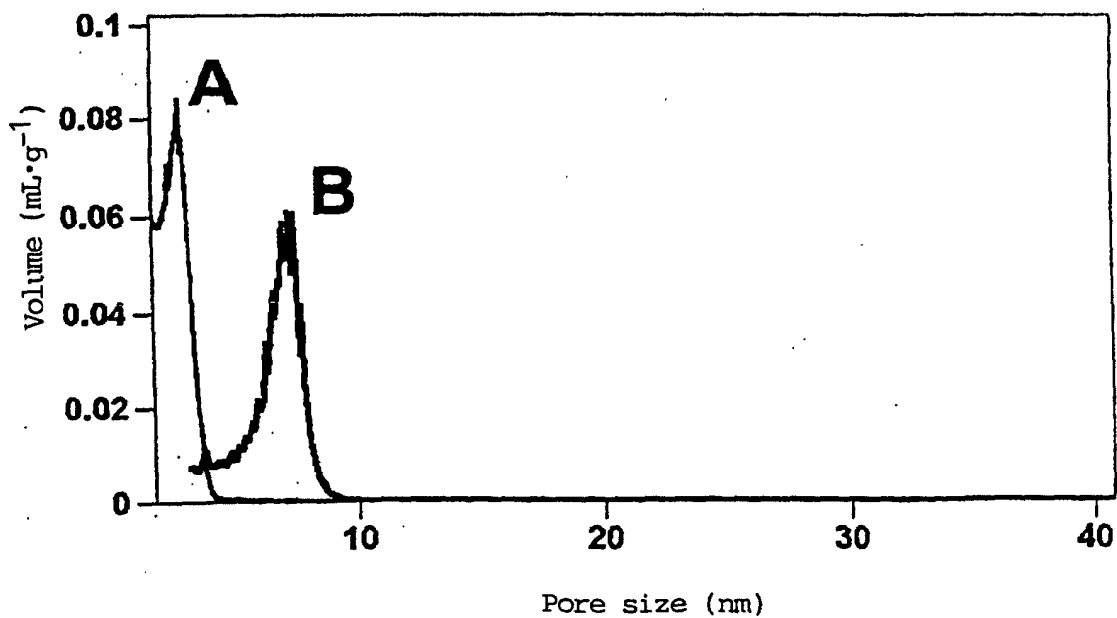


Fig.5

electron beam diffraction pattern of particle

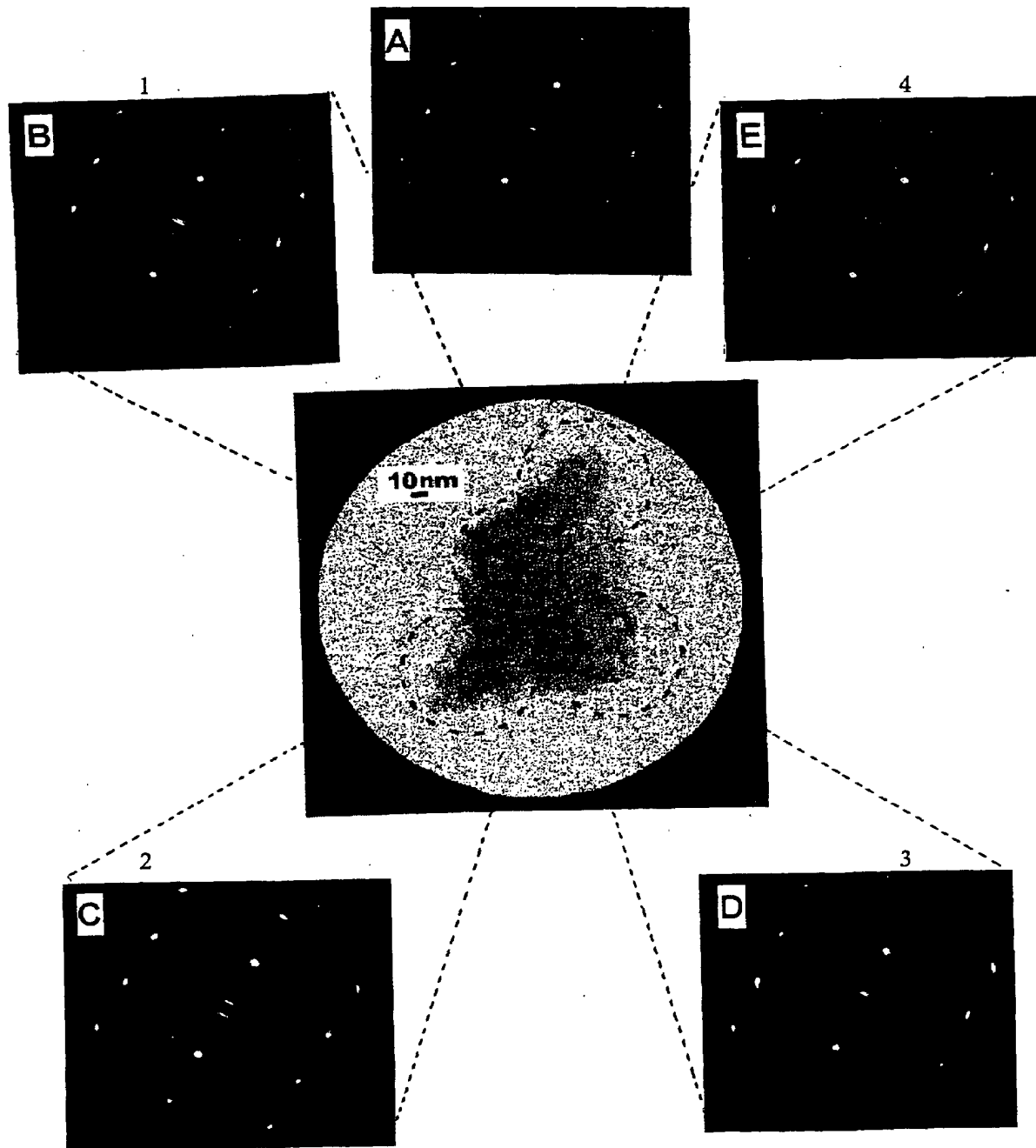
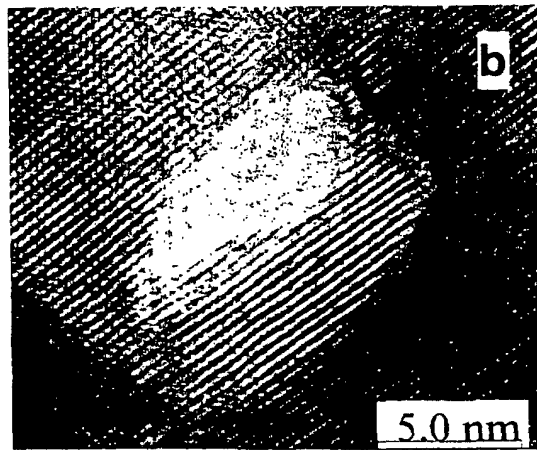


Fig.6



Transmission electron microscope image by high magnification

Fig.7

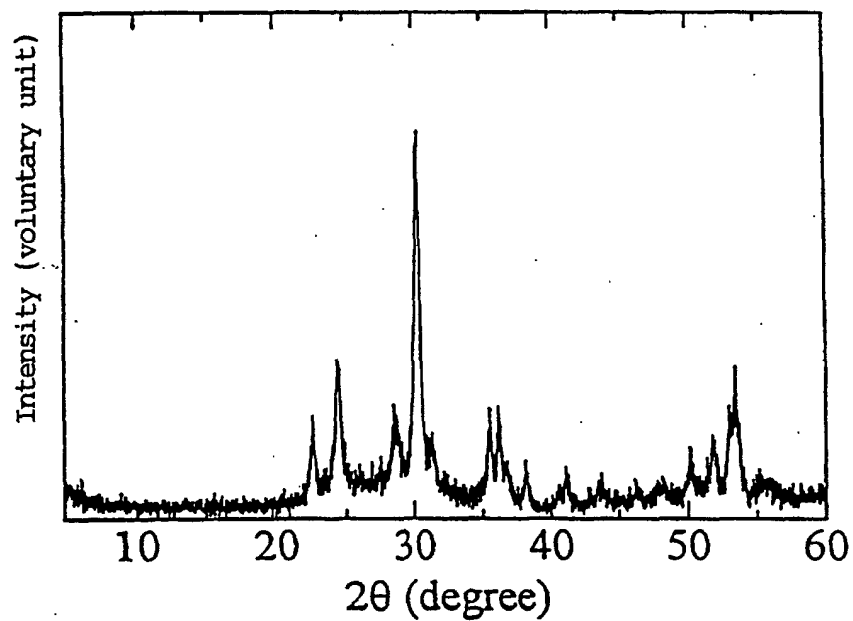


Fig.8

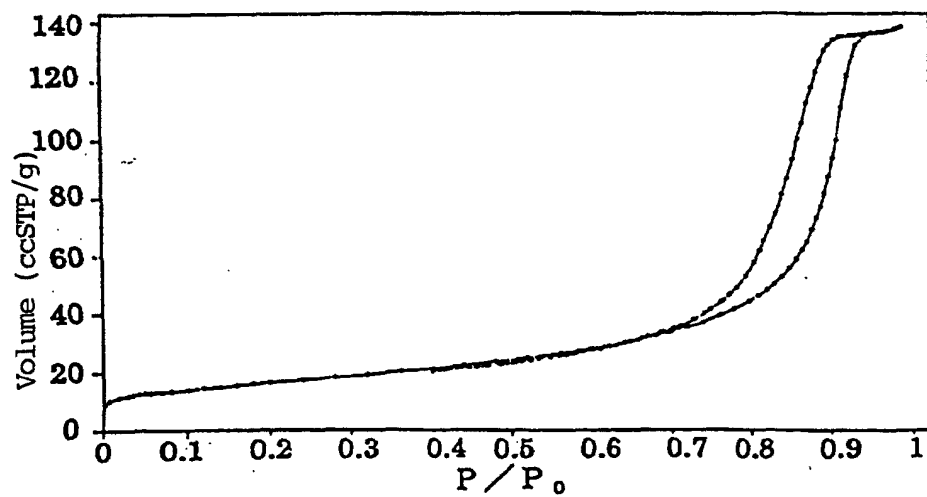


Fig.9

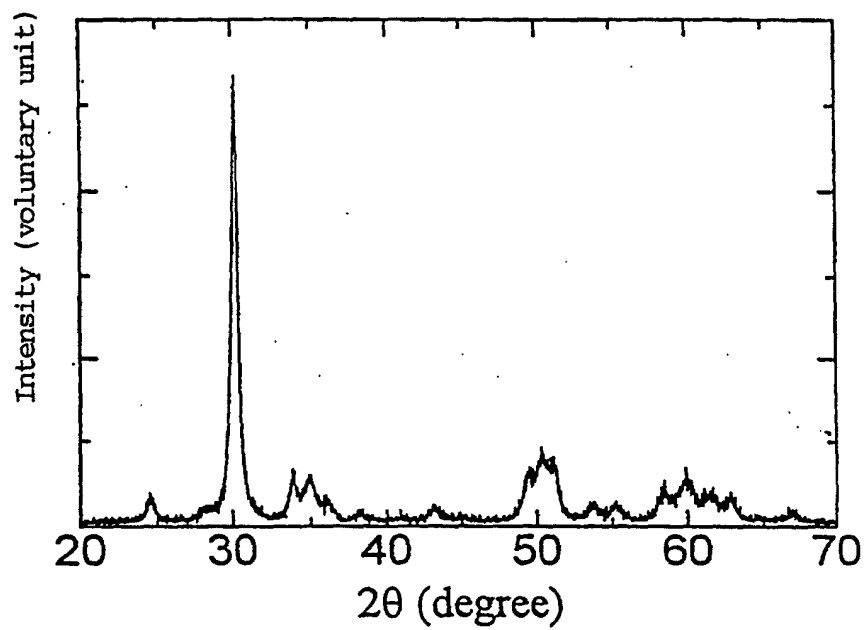
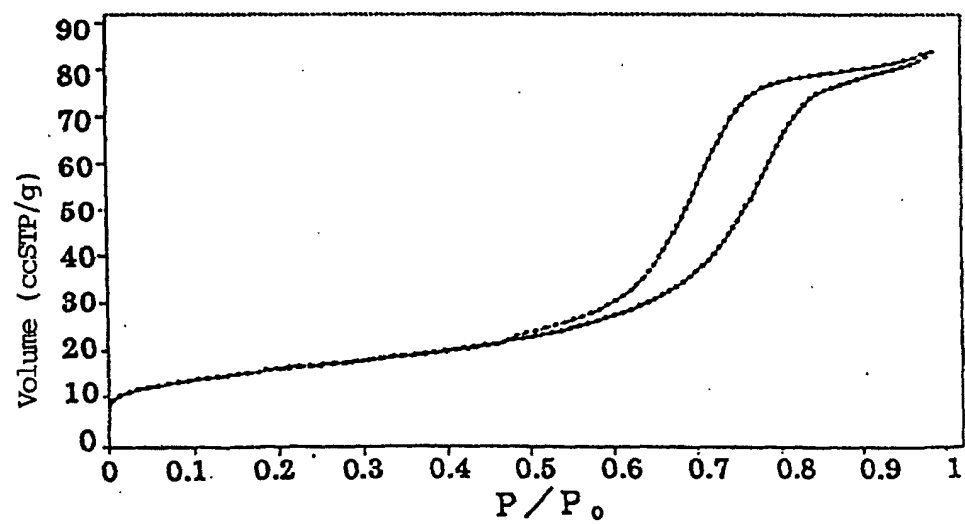


Fig.10



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/08266

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁷ C01G1/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ⁷ C01G1/00, C01G35/00, C01G33/00, C01B13/14		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2001 Kokai Jitsuyo Shinan Koho 1971-2001 Jitsuyo Shinan Toroku Koho 1996-2001		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
EX	JP, 2001-031422, A (Agency of Industrial Science and Technology), 06 February, 2001 (06.02.01), Claims; example (Family: none)	1-5
A	JP, 10-273320, A (Tokuyama Corp.), 13 October, 1998 (13.10.98), Claims; example (Family: none)	1-6
A	US, 5380691, A (RHONE-POULENC CHIMIE), 10 January, 1995 (10.01.95), Claims; example & JP, 3-50121, A (RHONE-POULENC CHIMIE), 04 March, 1991 (04.03.91), Claims; example & EP, 397553, A & FR, 2646943, A & DE, 69008412, E	1-6
A	JP, 11-079743, A (Natl Inst. for Res. in Inorg. Mater.), 23 February, 1999 (23.02.99), Claims; example (Family: none)	1-6
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 22 February, 2001 (22.02.01)		Date of mailing of the international search report 06 March, 2001 (06.03.01)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/08266

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 10-182144, A (Fine Ceramics Center), 07 July, 1998 (07.07.98), Claims; example (Family: none)	1-5

Form PCT/ISA/210 (continuation of second sheet) (July 1992)